

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

**A NON-PROVISIONAL APPLICATION**

**FOR**

**A NOVEL CARBON NANOTUBE LITHIUM BATTERY**

**CROSS REFERENCE TO RELATED APPLICATIONS**

This application claims priority to U.S. Provisional Application serial number 60/471,780, filed May 20, 2003.

**STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT**

This invention was made partially with U.S. Government support from the Office of Naval Research under contract number N0014-03-M0092. The U.S. Government has certain rights in the invention.

**FIELD OF THE INVENTION**

This invention pertains to energy storage devices. In particular, this invention relates to lithium-ion batteries having two active electrodes composed of carbon nanotubes, a battery separator and a lithium salt containing electrolyte.

**BACKGROUND OF THE INVENTION**

Future portable power requirements for consumer and military applications will demand greater specific energy and power from lithium battery technology. It is expected that in order to meet future power requirements, lithium batteries will need to exhibit sustained specific energies of  $> 400\text{Wh/kg}$  and have pulse power capability of  $> 2\text{kW/kg}$  @  $100\text{Wh/kg}$ . In addition, these systems will need to operate effectively over a wide temperature range ( $-20$  to  $90^{\circ}\text{C}$ ) and be capable of rapid recharge. These

requirements cannot be met by conventional batteries or through extrapolation of the capabilities of conventional systems. As is well known, the conventional Li-ion electrode materials are subject to physical chemical constraints which limit their lithium storage capability. For instance, mesocarbon microbeads (mcmb) are the best disordered carbon available for use in Li-ion anodes. At its peak, however, this material can only intercalate to  $\text{Li}_1\text{C}_6$  for a  $\text{Li}^+$  capacity of 372mAh/g. Carbon nanotubes are capable of intercalating to  $\text{Li}_1\text{C}_3$  or better at 1000mAh/g. Like mcmb, the lithium is intercalated reversibly so that the carbon nanotubes constitute a dramatic improvement over mcmb as an anode material.

Clearly, new materials need to be developed to meet these stringent future requirements.

#### SUMMARY OF THE INVENTION

The present invention relates to a high energy lithium battery system. This system comprises carbon nanotubes and/or other nanotubular materials for both the anode and cathode. The instant invention also pertains to methods for constructing these nanotubes. The instant invention relates to a battery that is comprised of two active electrodes each composed of carbon nanotubes, a battery separator and a lithium salt containing electrolyte. The separator and electrolyte can be any one of many well known to those skilled in the art. The liquid/solid polymer electrolytes of the present invention impart added safety to this high energy system. The carbon nanotube electrodes can be single wall, multiwall, nanohorns, nanobells, peapods, buckyballs and the like, or other colloquial names used to denote nanostructured carbon materials and combination thereof.

It is an object of the invention to describe high-energy electrode materials for lithium batteries.

Another object of this invention is to detail the processes required to prepare the high-energy materials of the instant invention.

Still another object of the invention is to describe a novel battery that utilizes the new electrode materials resulting in a very high specific energy battery capacity exceeding 200mAh/g.

Another object of the invention is to describe a means of forming a high-energy battery using a lithiated nanotube anode and a lithium metal oxide-doped nanotube cathode.

Another object of the invention is to demonstrate that various sources of lithium including lithium metal oxides can be used to lithiate a carbon nanotube anode.

Another object of the invention is to detail the composition of a high-energy battery comprised of two electrodes of carbon nanotubes wherein the structure of those electrodes is that of a paper-like material described as "buckypaper."

Another object of the invention is to describe the process for preparing the buckypaper electrodes.

Another object of the invention is to describe a novel battery architecture that utilizes the new electrode materials to provide a battery system with a specific energy exceeding 700Wh/kg.

Another object of the invention is to describe a novel battery architecture that utilizes the new electrode materials to provide a battery system with a specific power exceeding 3kW/kg.

Another object of the invention is to describe a battery system that can utilize various types of carbon nanotubes and nanotubular materials (A non-comprehensive list of examples include the colloquial named materials; nanobells, nanohorns, peapods, double-walled tubes *etc.*). Another object of the invention is to describe a combination of

the high-energy electrodes with a novel nonflammable polymer based electrolyte to yield a safe, ultra-high energy battery.

For a better understanding of the present invention, together with other and further needs thereof, reference is made to the accompanying drawings and detailed description and its scope will be pointed out in the appended claims.

#### BRIEF DESCRIPTION THE DRAWING

FIG. 1 is an illustration of an embodiment of the present invention;

FIG. 2 is an illustration of the general concept of the invention;

FIG. 3 is an illustration of various embodiments of the invention;

FIG. 4 is plot of the cycle behavior of a SWNT/SWNT battery;

FIG. 5 is a plot of the cycle behavior of a SWNT/fluorinated SWNT battery;

FIG. 6 is a plot of the cycle behavior of a MWNT/SWNT battery;

FIG. 7 is a plot of the effect of addition of  $\text{LiNiCoO}_2$  to a SWNT cathode in a battery;

FIG. 8 is a plot of the behavior of a SWNT/ $\text{LiNiCoO}_2$  coin cell battery; and

FIG. 9 is a plot of the behavior of SWNT battery.

#### DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to a high energy lithium battery system. This system comprises carbon nanotubes and/or other nanotubular materials for both the anode and cathode. In one embodiment, the instant invention relates to a battery that is

comprised of two active electrodes, each composed of carbon nanotubes, a battery separator, and a lithium salt containing electrolyte. The separator and electrolyte can be chosen from the many well known in the art. In the present invention, the liquid/solid polymer electrolytes impart added safety to this high energy system. In separate research efforts, the development of a new set of polyphosphate electrolytes that are safe, and possess enhanced thermal stability, have been studied.

Research efforts have identified polyphosphates and polyphosphonates (PEP) as good candidates for preparation of polymer electrolytes. See, for example, USSN 09/837,740, the entire teaching of which is incorporated herein by reference. In addition, success with both liquid and solid-state electrolyte systems has been realized. These novel materials are relatively inexpensive to prepare in a one step process and have yielded very good lithium ion transport properties of 0.5 as compared to 0.3 for polyethyleneoxide (PEO). Thermal stability testing has also yielded promising results (thermally stable to  $>300^{\circ}\text{C}$ ). To extend the operational temperature range from  $-20$  to  $+90^{\circ}\text{C}$ , we plan to blend our polyphosphate liquid electrolytes with propylene carbonate (PC) to enhance the low temperature performance of the polyphosphate materials. These liquids are completely miscible with polar liquids such as PC.

Synthesis of the PEPs is a straightforward, one-step process that minimizes product costs. Following synthesis of the polymers, a liquid polymer electrolyte (LPE) is prepared by dissolving a lithium salt at 1M concentration into the fluid polymer. The use of lithium bis-trifluoromethanesulfonimide (LiIm, 3M Co.) as the lithium salt in these electrolytes has been quite successful. The next step is to blend quantities of propylene carbonate into the LPE to form a modified LPE.

The carbon nanotube electrodes can be single wall, multiwall, nanohorns, nanobells, peapods, buckyballs and the like, or other colloquial names for nanostructured carbon materials and combinations thereof.

In another embodiment, methods for constructing the nanotubes of the present invention are described. In one aspect of this embodiment, a series of processing steps are described that are required to purify the nanotubes and open their structure. In this aspect, the anode is processed in a manner distinct from that of the cathode. Also, the electrochemical lithiation of the nanotube anode is described herein.

Portable power requirements for consumer and military applications demand greater specific energy and power from lithium battery technology. To meet these requirements, new concepts in lithium battery technology need to be conceived and developed. Nanostructured materials and polymer electrolytes offer new paths for development of higher energy lithium batteries.

In the area of electrode development, recent work with carbon nanotubes has opened the door to the first solid alternative to graphite as a high capacity anode material. Lithium intercalated graphite and other carbonaceous materials are commercially used as electrodes for advanced Li-ion batteries. See, for example, M. S. Whittingham, editor, *Recent Advances in Rechargeable Li Batteries*, Solid State Ionics, volumes 3 and 4, number 69, 1994; and D. W. Murphy *et al.*, editors, *Materials for Advanced Batteries*, Plenum Press, New York, 1980, the entire teaching of which is incorporated herein by reference. Most graphitic carbons offer a stoichiometry of  $\text{Li}_{0.3}\text{C}_6$  (375 mAh/g) whereas disordered carbons are generally  $\text{Li}_1\text{C}_6$  (400 mAh/g). In comparison to lithiated carbon, lithium metal anodes have a theoretical capacity of > 3000 mAh/g and a practical capacity of 965 mAh/g.

Carbon nanotubes have attracted attention as potential electrode materials. Carbon nanotubes often exist as closed concentric multi-layered shells or multi-walled nanotubes (MWNT). Nanotubes can also be formed as single-walled nanotubes (SWNT). The SWNT form bundles, these bundles having a closely packed 2-D triangular lattice structure. Both MWNT and SWNT have been produced and the specific capacity of these materials has been evaluated by vapor-transport reactions. See, for example, O. Zhou *et al.*, *Defects in Carbon Nanotubes*, Science:263, pgs. 1744-47, 1994;

R. S. Lee *et al.*, Conductivity Enhancement in Single-Walled Nanotube Bundles Doped with K and Br, *Nature*: 388, pgs. 257-59, 1997; A. M. Rao *et al.*, Raman Scattering Study of Charge Transfer in Doped Carbon Nanotube Bundles, *Nature*: 388, 257-59, 1997; and C. Bower *et al.*, Synthesis and Structure of Pristine and Cesium Intercalated Single-Walled Carbon Nanotubes, *Applied Physics*: A67, pgs. 47-52, spring 1998, the entire teaching of which is incorporated herein by reference. The highest alkali metal saturation values for these nanotube materials was reported to be  $MC_8$  ( $M=K, Rb, Cs$ ). These values do not represent a significant advance over existing commercially popular materials, such as graphite. Recent experimental results have shown that it is possible to charge single wall carbon nanotubes up to  $Li_1C_3$  and higher. Capacities of crude material have been determined experimentally to exceed 600 mAh/g. These capacities begin to approach that of pure lithium, but avert lithium's safety concerns. Clearly, carbon nanotubes offer new prospects for high-energy batteries and can offer new opportunities for completely new battery designs hitherto unattainable with conventional electrode materials.

The lithiated carbon nanotubes have been reported in the scientific and patent literature as a means for providing a high energy, non-metallic anode for lithium batteries. In particular, Zhou, US Pat Nos. 6280697, 6422450 and 6514395, the entire teaching of which is incorporated herein by reference, describes in detail the processes for preparing laser generated carbon nanotubes and their lithiation. However, the prior art does not include the concept of using a lithiated nanotube anode and a non-lithiated nanotube cathode to form a high energy battery nor does it describe a means of modifying the cathode by addition of lithium metal oxides to increase the cell voltage. Also, the prior art does not describe doping nanotube cathodes or anodes with modifying conducting materials, such as conducting polymers, or fluorinating one nanotube electrode before combination with a second, chemically-distinct nanotube electrode to form a battery.

Conventional, commercial lithium-ion battery technology relies on lithiated metal oxides for the positive electrode (cathode) and carbon (of various forms) as the negative

electrode (anode). A Li-ion cell begins life with all of the lithium in the cathode and upon charging, a percentage of this lithium is moved over to the anode and intercalated within the carbon anode. When the charging process is finished, the cell has an open circuit voltage of approximately 4.2V. Approximately 1.15V of this cell voltage is due to the positive potential of the metal oxide electrode. The diverse chemistry of these two materials ensures a high open circuit potential. It is conceivable, however, to use materials with similar chemistries to affect a similar result. In 1980, the "rocking chair concept", *i.e.*, using two insertion compounds based on metallic oxides or sulfides, was proposed by Lazzari and Scrosati (M. Lazzari and B. Scrosati, *J. Electrochem. Soc.*, Brief Communication, March 1980, the entire teaching of which is incorporated herein by reference). A  $\text{Li}_x\text{WO}_2/\text{Li}_y\text{TiS}_2$  cell was described, working at an average voltage of 1.8 V. While this system could solve the metallic lithium anode problems, it was unable to provide the practical energy density required to make it a viable alternative to existing rechargeable systems. Following this preliminary report, workers moved away from using two metal oxide electrodes having found that certain types of carbon could reversibly intercalate lithium. Most graphitic carbons offer a stoichiometry of  $\text{Li}_{0.3}\text{C}_6$  (375 mAh/g) whereas disordered carbons are generally  $\text{Li}_1\text{C}_6$  (400 mAh/g). In comparison to lithiated carbon, lithium metal anodes have a theoretical capacity of > 3000 mAh/g and a practical capacity of 965 mAh/g (Linden, D. and Reddy, T.B., *Handbook of Batteries*, 3<sup>rd</sup> ed. p34.8, McGraw-Hill, NY, 2001, the entire teaching of which is incorporated herein by reference).

The present invention relates to a battery that is comprised of two active electrodes each composed of one or more carbon nanotubes, a battery separator and a lithium salt containing electrolyte. The separator and electrolyte can be any one of many well known to those skilled in the art. The liquid/solid polymer electrolytes of the present invention will impart added safety to this high energy system. The carbon nanotube electrodes can be single wall, multiwall, nanohorns, nanobells, peapods, buckyballs and the like, or other colloquial names for nanostructured carbon materials and combinations thereof.



Throughout this description it should be understood that the general term carbon nanotubes or nanotube refers to the whole series of carbon nanotubular materials well known to those skilled in the art. In addition, the nanotubes can be combined with lithium metal oxides to increase cell voltage or can be chemically-doped with conducting materials such as conducting polymers, thermally oxidized or fluorinated to affect the work function of the nanotube and thereby increase cell voltage. In general, the nanotube electrodes of this invention require specific processing as detailed herein.

In one embodiment of the present invention, a lithium-ion (Li-ion) battery that utilizes carbon nanotubes with different lithium activities for both the anode and cathode is described. In one aspect, this invention pertains to the use of a buckypaper structure of carbon nanotubes as the electrodes. In this aspect, the materials are formed by filtering suspensions of carbon nanotubes onto inert filter media and then drying and oxidizing the material in air. The technique has been well documented in the scientific literature, but until now, there have been no reports of a battery in which a buckypaper comprises both electrodes - there have been no reports indicating the use of carbon nanotube buckypapers for both electrodes in a battery.

Figure 1 illustrates an embodiment of the present invention. The battery system 1 depicted within this figure includes an anode 3, a cathode 5, a separator 7, and means 8 for facilitating electrical communication between the anode 3 and the cathode 5. In one aspect of this embodiment, the anode 3 and/or cathode 5 are comprised of carbon nanotube material. The carbon nanotube material can be multi-walled, single-walled, nanohorns, nanobells, peapods, buckyballs or any other known nanostructured carbon material. The anode 3 is a  $\text{LiC}_3$  anode and the separator 7 comprises, *e.g.*, Li salt and solvent. The separator 7 comprises an insulating material(s) having a liquid or polymer cation conducting electrolyte. The means 8 for electrically communication between the anode 3 and the cathode 5 includes any means well known in the art that facilitates electrical communication between an anode and cathode. Such means include, but not limited to, a suitably low resistance wire.

Figure 2 is useful for summarizing the contrasts between a conventional lithium-ion technology (FIG. 2 a + b) with that of the instant invention (FIG. 2 c + d) to illustrate the overall concept of the present invention. In this drawing, the conventional Li-ion system 9 comprises a mesocarbon microbead (mcmb) anode 11 and a  $\text{LiNiCoO}_2$  cathode 13, a standard separator and electrolyte (not shown, see FIG. 1). A Li-ion cell 9 begins life with all of the lithium in the  $\text{LiNiCoO}_2$  cathode 13. Upon charging (FIG. 2a), approximately 98% of this lithium is moved over to the mcmb anode 11 and intercalated within the carbon anode 11. When the charging process is finished, the cell 9 has an open circuit voltage of approximately 4.2V. Approximately 1.15V of this cell voltage is due to the positive potential of the metal oxide electrode 13. Upon discharge, the lithium that was previously intercalated in the mcmb anode now transits the electrolyte and is re-deposited in the spinal structure of the  $\text{LiNiCoO}_2$ .

By contrast, the cell 9' of the instant invention begins with a lithiated SWNT anode 11' that has been suitably processed prior to lithiation. (The details of this processing are included in Example 3, *infra*.) By way of example, but not by way of limitation, lithiation can be accomplished galvanostatically employing a lithium foil and suitable apparatus well known to those skilled in the art. The SWNT cathode 13' is processed in a particular manner distinct from that of the anode. This imparts very different chemical and physical properties to the cathode 13'. When assembled (FIG. 2c + d), the cell 9' contains a separator and an electrolyte (both not shown) and has a voltage of from about 2.9 to 3.5V depending on the processing of the two electrodes. Upon discharge (FIG. 2c), the lithium cations move from the anode 11' to the cathode 13' and the cell voltage decreases. Reversing the current to charge the cell 9' moves the lithium cations back to the anode 11' restoring the cell voltage. See FIG. 2d. The processing of the two materials is critical to keeping the cell voltage intact.

The important concept for the instant invention is a Li-ion battery that utilizes carbon nanotubes with different lithium activities for both the anode and cathode. Figure 3 details a number of approaches that can constitute the embodiment of the instant invention.

One approach as shown in FIG. 3a centers on using two different types of nanotubes selectively for the anode and cathode. By way of example, but not by way of limitation, the use of SWNTs as the positive electrode and lithiated multiwalled carbon nanotubes (MWNTs) as the negative electrode is described. This cell will begin life with the lithium residing in the MWNT electrode and upon charging the  $\text{Li}^+$  will be moved to the SWNT electrode. In this instance, the work function of the MWNTs is higher than that of the SWNTs. As a result, lithiating the MWNTs first will lead to a higher cell voltage upon discharge, which is advantageous. The reversal of this architecture would still result in a workable cell, but one that is somewhat less desirable from an efficiency standpoint. One can chemically or electrochemically lithiate the MWNT electrode prior to assembly of the cell. One approach is to electrochemically lithiate the SWNT material using a pure lithium counter electrode and an appropriate electrolyte and separator. In one embodiment, the material is lithiated at a low rate ( $< 100 \text{ microA/cm}^2$ ) for long periods of time ( $\sim 20 \text{ hrs}$ /0.5mg of material). This arrangement results in a cell voltage of  $\sim 3.0 \text{ V}$  before charge and  $\sim 3.2 \text{ V}$  for the fully charged cell. When charged, the lithiated MWNT anode will have a voltage of  $\sim -3 \text{ V}$  vs the normal hydrogen electrode (NHE) while the SWNTs should have a voltage of  $\sim +0.15 \text{ V}$  vs NHE by virtue of the higher work function of SWNTs vs MWNTs. Although the relationship between the work function of an electrode and its reversible potential in a system is complex, Trassasti (Trassati, S., *Electroanal Chem and Interfac Electrochem.* 33, 351-78, (1971), Trassati, S. *Surface Sc*, 335, 1-9, (1995), the entire teaching of which is incorporated herein by reference), has written extensively about this relationship that describes a general rule that the lower the work function of an electrode, the lower its potential vs NHE.

However, the activity of the electrolyte must be considered as well, so it may be that the difference in work function between the MWNTs and the SWNTs may result in a higher electrode voltage for the SWNT vs  $\text{Li/Li}^+$ . Shiraishi (Shiraishi, M. and Ata, M., *Mater Res. Soc. Sympos. No. 633*, A4.41, Mater. Res Soc., Pittsburgh, PA. 2001, the entire teaching of which is incorporated herein by reference) has reported the work

function of SWNTs to be 0.15eV higher than that for MWNTs. Therefore, a voltage difference of at least 150mV between these materials can be expected.

An alternative approach is depicted in FIG. 3b where SWNTs are chemically modified by fluorination, but other oxidation processes such as chlorination could also be used. This process affects the work function of the carbon nanotubes and further enhances the full cell voltage. For example, Touhara, *et al.* (Touhara, H., *et al.*, J Fluorine Chemistry, 114, 181-88, 2002, the entire teaching of which is incorporated herein by reference) recently reported that fluorination of the inner surface of carbon nanotubes leads to improved Li<sup>+</sup> intercalation and a 660 mV increase in the OCV of electrodes composed of fluorinated nanotubes immersed in aprotic electrolytes. This combination of higher work function and chemical modification can be the key to increasing the cell voltage of the LiSWNTs/SWNTs lithium-ion battery. The result would be a very high capacity, > 3V lithium-ion battery.

Another approach as seen in FIG. 3c for chemical modification lies in treating the SWNTs with an organic conducting material, for example, a conducting polymer such as poly3-octylthiophene as an example. Other conducting polymers could also be used for this purpose. By way of example members of this group could include: substituted polythiophenes, substituted polypyrroles, substituted polyphenylenevinyls, and substituted polyanilines. Ion doping of these materials or self-doping, by including a sulfonic acid group at the end of the alkyl chain, will render the conducting polymer p-type. Again, this treatment alters the work function of the nanotubes and thereby increases the full cell voltage.

As another alternative, as shown in FIG. 3d, it is possible to incorporate lithiated nanotubes in place of carbon black with the metal oxide materials currently used as the active cathode material in Li-ion batteries. This would have a two-fold advantage: 1) the nanotubes would offer higher electronic conductivity to the resulting composite electrode thereby improving cathode performance and 2) the lithiated nanotubes would

dramatically improve the capacity of the cathode. The high cell voltage would be preserved by the presence of lithium metal oxides in the cathode.

Another possible combination is to utilize a lithiated SWNT anode material and a cathode comprised of pure SWNTs as depicted in FIG. 3e. In this scenario, the SWNT anode material would be processed in a manner different from that of the SWNT cathode material. By way of example, but not by way of limitation, the anode SWNT material could be refluxed in dilute mineral acid, washed with water and acetone and then thermally oxidized using select gases, as an example, CO<sub>2</sub>. By contrast the SWNT cathode materials could be refluxed in dilute mineral acid and then thermally oxidized in air.

Another possible combination is to utilize a lithium composite anode such as LiSiC material as described in the scientific literature (Yang, J., *et al.*, Electrochemical and SolidState Letters, 6 (8), A154-A156 2003, the entire teaching of which is incorporated herein by reference) anode material and a cathode comprised of pure SWNTs as depicted in FIG. 3f. In this example, the SWNT cathode materials could be refluxed in dilute mineral acid and then thermally oxidized in air and would afford high capacity to compliment the high capacity of the LiSiC composite.

## EXAMPLES

The following examples are meant to illustrate the concept of the instant invention, they are not intended to limit the scope of the invention.

### Example 1

To illustrate the basic concept of a SWNT/SWNT battery, a batch of SWNTs was prepared using the laser ablation techniques that is well known to those skilled in the art. For example, one suitable technique for producing SWNT bundles is described in C. Bower *et al.*, Synthesis and Structure of Pristine and Cesium Intercalated Single-Walled

Carbon Nanotubes, Applied Physics: A67, pgs. 47-52, spring 1998 or as described in US Patent 6,422,450, the entire teaching of which is incorporated herein by reference.

Following synthesis of a batch of this SWNT material, the material was processed to purify it by reflux in 5%  $\text{HNO}_3$  for 15 hours, followed by extensive washing with deionized water. The final product was then collected by filtration on an inert, porous Teflon filter. The product was then air dried at  $100^\circ\text{C}$  for 15 hours which resulted in a buckypaper. From this buckypaper a  $1\text{cm}^2$  electrode was cut and placed in a two electrode test cell in which contained one piece of Celgard 2350 porous polypropylene separator and a 1M lithium bis-trifluoromethanesulfonimide (LiIm) in 50:50 ethylene-carbonate:ethylmethyl carbonate (EC/EMC) electrolyte. All of the electrodes were weighed before cell assembly using a Mettler UMT-2 microbalance. All of these steps were conducted in an Ar-filled glovebox. A lithium pure foil served as the counter electrode and the SWNT anode was lithiated by passing a  $100\text{ }\mu\text{A}/\text{cm}^2$  current through the cell for 10 hours. Following this procedure, the cell was disassembled, cleaned and reassembled with the lithiated anode a new separator and a pure SWNT cathode. The cathode material had been processed in the same manner as the anode materials except that it was then heated in air at  $500^\circ\text{C}$  for one hour. The complete cell was then cycled by passing  $100\text{ }\mu\text{A}/\text{cm}^2$  of negative current through the cell (anode is positive cathode negative) and then  $100\text{ }\mu\text{A}/\text{cm}^2$  of positive current to cycle the  $\text{Li}^+$  from electrode to electrode. The result of this procedure is illustrated in FIG. 2 which shows that the cell voltage varies with time under the load, but the lag is quite extensive such as one that would be normally associated with a Faradaic process. Based on the weight of the material used and the current used, one can then calculate the specific energy of this system as summarized in Table 1.

Table 1 SWNT Battery Behavior

Cell	Ave. Discharge Voltage (@ 100 $\mu$ A)	Ave. Discharge Voltage (@ 50 $\mu$ A)	Whr	Electrode weight (mg)	Specific Energy (Wh/kg)
NT2-4		3.13	$7.82 \times 10^{-5}$	1.2 ( $1.2 \times 10^{-6}$ kg)	78
NT2-8		1.81	$2.72 \times 10^{-4}$	1.2 ( $1.2 \times 10^{-6}$ kg)	220

As shown in Table 1, the first series of tests with this cell yielded a specific energy of 78Wh/kg. Subsequent to this test, a second cell was prepared in which the anode was treated in the same fashion, but during the washing processes following acid reflux, a step was added in which the SWNT material was washed with acetone following the water wash. Otherwise, the sample was treated identically to the first sample. The result for this anode material was considerably better than the first result with the sample exhibiting a specific energy of 200Wh/kg. These results firmly establish the validity and uniqueness of the instant invention.

#### Example 2

To further illustrate the unique properties of the instant invention, a comparison was made between similar carbon/carbon batteries comprised of standard mesocarbon microbead (mcmb) materials in which one mcmb electrode was lithiated while another was not. Lithiation of the mcmb anode was conducted by passing  $100 \mu\text{A}/\text{cm}^2$  from a pure lithium anode in a test cell containing a separator and a lithium salt electrolyte for up to 20 hours. In a similar manner, a SWNT anode was lithiated. Following the lithiation, the two test cells were cleaned and then reassembled. In the mcmb control cell, a fresh mcmb electrode was used as the cathode. In the SWNT cell, a pure SWNT buckypaper was used as the cathode. All of the electrodes were weighed before cell assembly using a Mettler UMT-2 microbalance. The cells were each individually discharged at a set current density ( $100 \mu\text{A}/\text{cm}^2$ ) and subsequently cycled. All of these steps were conducted in an Ar-filled glovebox. The same procedure was used for a control test in which mcmb

was substituted for SWNT material. The mcmb anode and cathode each weighed 15 mg, the usual weight for the SWNT electrodes was between 0.6 to 1 mg. A comparison of the output of these two cells is summarized in Table 2 below.

Table 2, Comparison of mcmb Control and SWNT Battery

Cell	Ave. Discharge Voltage (@ 100 $\mu$ A)	Ave. Discharge Voltage (@ 50 $\mu$ A)	Whr	Electrode weight (mg)	Specific Energy (Wh/kg)
mcmb	2.89		$1.45 \times 10^{-4}$	30 ( $3 \times 10^{-5}$ kg)	4.8
NT2-4		3.13	$7.82 \times 10^{-5}$	1.2 ( $1.2 \times 10^{-6}$ kg)	78
NT2-8		1.81	$2.72 \times 10^{-4}$	1.2 ( $1.2 \times 10^{-6}$ kg)	220

As shown, the SWNT cell appears to offer better performance over the course of the discharge. In this test the SWNT anode was an acid reflux sample and the cathode was a pure SWNT paper. The specific energy of these two materials were calculated and compared. Referring to these results, it is evident that the SWNT cell offers a much higher specific energy (78Wh/kg) than the mcmb control. This indicates that the SWNT battery is far more energetic than the control, highlighting the special properties of carbon nanotubes. In addition, this result clearly shows the unique properties of the SWNT battery.

### Example 3

By way of example, but not by way of limitation, as a means of further improving on the capacity of the SWNT anode materials, the tubes were shortened by selective oxidation in a slightly oxidative atmosphere such as carbon dioxide (CO<sub>2</sub>). Although carbon dioxide was employed as the oxidant, one could also utilize other oxidative gases such as but not limited to: CO, NO, NO<sub>2</sub>, N<sub>2</sub>O, O<sub>3</sub>, SO<sub>2</sub>, peroxides, ethylene oxide and the like.



The SWNT material is heated from 600-1000°C under flowing oxidative gas for an appropriate time period of 1.5 hours. The oxidative atmosphere can oxidize any remaining carbonaceous materials and introduce limited defect sites that exist on the SWNT backbone. Some shortening and functionalization of the SWNTs can result. Increases and decreases in pore size, particle size and surface area also can occur. The process starts and ends with a freestanding buckypaper.

To illustrate the benefits of this treatment, two additional tests were conducted using a oxidizing gas treated SWNT sample as the lithiated anode and a pure SWNT cathode. The control for these experiments was a standard Li-ion cell comprised of an mcmb anode a  $\text{LiNiCoO}_2$  cathode a separator and a lithium salt electrolyte. The control was charged at  $0.1\text{mA}/\text{cm}^2$  for 12 hours and then discharged at  $100\text{ mA}/\text{cm}^2$ . The SWNT anode was lithiated in the usual manner beforehand and then the cell was assembled in the usual manner. All of these steps were conducted in an Ar-filled glovebox. Figure 4 summarizes the cycle results for the SWNT cell and illustrates that this cell could be successfully cycled many times. Table 3 summarizes the comparison between the control cell and the two SWNT test cells.

Table 3: Comparison of two distinct Rocking Chair-SWNT battery test-cells versus an mcmb Li-ion control.

Cell	Av Voltage @100mA/cm <sup>2</sup>	Av Voltage @ 50 mA /cm <sup>2</sup>	Wh	Active material wt (mg)	Specific Energy (Wh/kg)
NTx2-30		1.94 2.10 2.10	8.50x10 <sup>-5</sup> 1.82x10 <sup>-4</sup> 1.24x10 <sup>-4</sup>	0.30 (3x10 <sup>-7</sup> kg) 0.30 (3x10 <sup>-7</sup> kg) 0.30 (3x10 <sup>-7</sup> kg)	285 2 <sup>nd</sup> cycle 606 4 <sup>th</sup> cycle 414 8 <sup>th</sup> cycle
NTx2-37		2.39 2.78 2.33	6.00x10 <sup>-5</sup> 6.95x10 <sup>-5</sup> 1.17x10 <sup>-4</sup>	0.197(2x10 <sup>-7</sup> kg) 0.197(2x10 <sup>-7</sup> kg) 0.197(2x10 <sup>-7</sup> kg)	309 1 <sup>st</sup> cycle 360 3 <sup>rd</sup> cycle 603 6 <sup>th</sup> cycle
Li-ion	3.43		4.36x10 <sup>-3</sup>	30.0 (3x10 <sup>-5</sup> kg)	145

As shown in Table 1, both of the SWNT test cells exhibit superior specific energy than the standard mcmb control. A second control experiment was conducted using two mcmb electrodes cut from a commercial anode supplied by Yardney Technical Products (Pawcatuck, CT.) where one electrode was pre-lithiated, and the other was not. This control establishes the oxidized SWNT material as being unique in its properties to reversible intercalate lithium in a rocking chair battery in comparison to conventional disordered carbon. The mcmb anode and cathode each weighed 15 mg, the usual weight for the SWNT electrodes was between 0.1 to 1 mg. This impressive performance was verified with a second sample where we observed increases from 309 to 603 Wh/kg from the 1<sup>st</sup> to 6<sup>th</sup> cycles. It is important to note that since the first set cycles were not allowed

to fully discharge, *i.e.*, a switch was effectuated based on time (1 hour), not voltage, the performance would actually be better than the values reported.

#### Example 4

As another example of the instant invention, a battery configuration of a lithiated MWNT anode vs. a pure SWNT cathode was successfully tested. This sample of MWNT was obtained from a batch synthesized according to the CVD process. The multiwalled carbon nanotubes were prepared by the injection chemical vapor deposition (CVD) method using cyclopentadienyliron dicarbonyl dimer as the iron catalyst source, J. D. Harris, A. F. Hepp, R. Vander Wal, B. J. Landi, R. P. Raffaele, T. Gennett, "Organometallic Catalysts for Injection Chemical Vapor Deposition of Carbon Nanotubes", submitted for publication, the entire teaching of which is incorporated herein by reference. Toluene was used as the solvent. These as-produced MWNTs were only 3% w/w iron, and; therefore, were used without any further attempts to remove the metal.

A MWNT buckypaper electrode was prepared from this as-produced material via dispersion in an aqueous surfactant solution. After oxidation in a carbon dioxide atmosphere, a portion of that electrode was cut to size and then lithiated in the usual fashion. Since the MWNTs are known to have a decreased lithium ion capacity as compared to SWNT materials, the mass of the MWNT electrode was increased to 800 mg versus the 200 mg pure SWNT cathode. Finally, a MWNT-SWNT cell was assembled and the tested according to the previously outlined protocol. The cell was charged at  $100 \mu\text{A}/\text{cm}^2$ , discharged at  $50 \mu\text{A}/\text{cm}^2$  and as can be seen in the 9 sets of cycles illustrated in FIG. 5, the performance improved with time from 130 to 250 Wh/kg. Although the performance of this cell was slightly reduced from the SWNT cell, the results illustrate that the anode in this cell can be composed of commercially available MWNT material. This shows that when processed correctly and using our pre-lithiation techniques, commercially available mutli-wall nanotube material can also be used successfully in our nanotube rocking chair battery configuration.

### Example 5

As a further example of this instant invention, a cell containing a fluorinated nanotube anode (f-SWNT) was tested. In this case both commercially available and specially prepared f-SWNTs were used. In the first case, a f-SWNT anode was prepared using material obtained from CNI, Inc (Boston, MA). In addition, a second cell was prepared with a nanotube sample prepared using our typical CO<sub>2</sub> procedure which was subsequently fluorinated by Prof. John Margrave at Rice University. This process has been described in the literature (Khabashesku, V. N.; Billups, W.E. and Margrave, J.L., *Accts. Of Chem Res.*, 35, (2), 1087-1095, 2002, the entire teaching of which is incorporated herein). The fluorinated CNI-SWNTs were designated CF<sub>2</sub> while the second sample was analyzed to CF<sub>0.6</sub>. These samples were all lithiated and cycled using our standard techniques. For the CNI sample, CF<sub>2</sub> sample the lithium capacity of the fluorinated SWNT material was high, but the anode did not exhibit good cycle characteristics nor high specific energy. The fluorination did, however increase the cell voltage as expected, due to the higher oxidation potential of the fluorinated SWNT material (H. Peng, Z. Gu, J. Yang, J.L. Zimmerman, P.A. Willis, M.J. Bronikowski, R.E. Smalley, R.H. Hauge, J.L. Margrave, *Nanoletters*, 1, 625-629 (2001); V.N. Khabasheku, W.E. Billups, J.L. Margrave, *Acc.Chem. Res.*, 35, 1087, (2002), the entire teaching of which is incorporated herein by reference). With the CF<sub>0.6</sub> sample, in a configuration with the fluorinated nanotubes as the cathode and lithiated carbon dioxide processed SWNTs as the anode, displayed a performance comparable to our SWNT-Pure SWNT, however similar to the literature results, the interaction of the lithium ions with the fluorine introduces a significant amount of hysteresis that was not present for the carbon dioxide processed samples. Therefore, the introduction of the fluorine does slightly improve overall cell performance, but the increased complexity and costs associated with fluorination limit the application of the system.

### Example 6

As another example of this novel invention, a single cell battery using a lithiated SWNT anode and a pure SWNT cathode with a nonwoven glass paper separator (Hollingsworth and Vose BG03010) and a 1M LiIm in a polyether phosphate (PEP) electrolyte containing 20%ethylene carbonate was prepared. The PEP liquid polymer is the subject of patent application 09/837,740 to Morris *et al.*, the entire teaching of which is incorporated herein by reference, and has been shown to be a flame retardant material even when modified with carbonates such as ethylene carbonate. This cell was assembled and cycled and yielded the following results in discharge:

Current (microamps)	Cycle Number	Terminal cell voltage (V)
50	3	3.2
100	3	3.2
200	3	2.9
300	3	2.5

The cell performance was nearly as good as the liquid electrolyte test cells.

### Example 7

As a further example of the flexibility of the instant invention, a cell was fabricated using a lithiated SWNT buckypaper and a pure SWNT cathode laced or doped with a lithium metal oxide. The objective was to increase the voltage of the test cell by including a lithium metal oxide with a higher oxidation state than the SWNT material. By way of example, by not by way of limitation,  $\text{LiNiCoO}_2$  was chosen for use, but any other lithium metal oxide of which there are many current popular representatives could be used in this manner to increase the voltage of the cathode in the test cell. Following cell assembly, the cell was cycled which yielded the results exhibited in FIG. 7. As shown in the FIG. 7, the cell that contained a lithiated SWNT anode and a pure SWNT

cathode yielded a lower cell voltage than the cell that contained the LiNiCoO<sub>2</sub>-doped SWNT cathode.

#### Example 8

Further verification of the small cell results was obtained at RIT (Rochester Institute of Technology) when several coin cells were fabricated and tested employing LiNiCoO<sub>2</sub> cathodes and a non-optimized SWNT buckypaper (acid refluxed, water washed, dried at 250°C). The cells were cycled and also subjected to pulse power tests.

The typical charge/discharge behavior for the nanotube anode coin cells tested is shown in FIG. 8. The battery was charged using a constant current of 100  $\mu\text{A}/\text{cm}^2$  until it reached a voltage of 4.2V at which point it was switched over to a 100  $\mu\text{A}/\text{cm}^2$  discharge current. The battery was then discharged to a voltage of 2.0V at which point it was switched to charging once again. The first discharge cycle had a capacity of 166mAh/g of nanotube material under these conditions.

Similar to the results in the battery test cell, the cell capacity of the coin cell increased with cycling. A cell which utilized a CO<sub>2</sub> processed laser generated single wall carbon nanotubes and exhibited a capacity of less than 100mAh/g after its first cycle, but in excess of 500mAh/g after 6 cycles.

#### Example 9

During the investigation the sample 1 cell was also evaluated to determine its pulse power characteristics. Figure 6 shows that for this one pulse, the SWNT-cell maintained better than 1 Volt for 1.25 seconds at 1milliampere discharge. See FIG. 9.

Since the active material weighed 0.3 mg, and the average voltage during discharge was 1.38V, this yielded a peak pulse power output of 4.6kW/kg. Although this

result is only based on the mass of active materials, it demonstrates that it is possible to obtain both high specific power and specific energy from one SWNT-based system.

Although the invention is described with respect to various embodiments, it should be realized that this invention is also capable of a wide variety of further embodiments within the spirit and scope of the appended claims.